

CO₂ Removal using a Synthetic Analogue of Carbonic Anhydrase

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Program Team

- Hamilton Sundstrand
Review of CO₂ separations system testing



- Columbia University
*Modification of Synthetic Analogue
(Prof. Gerard Parkin's group)*



- WorleyParsons, LLC
*Review of power plant -coupled system
performance and cost models*



- CM-Tec, Inc.
Custom Chemical Synthesis



- GL Chemtec Int'l, Ltd.
Custom Chemical Synthesis



- Consultants:



Prof. Benny Freeman
University of Texas



Prof. William Koros
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Prof. Don Paul
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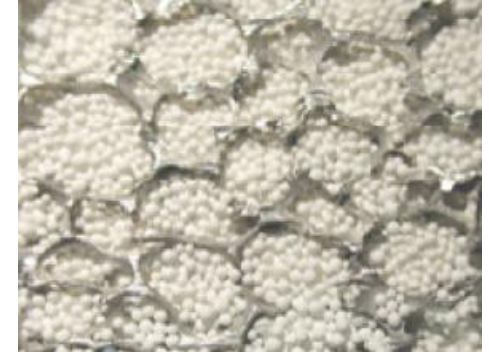


Prof. E. Bryan Coughlin
UMass (Amherst)

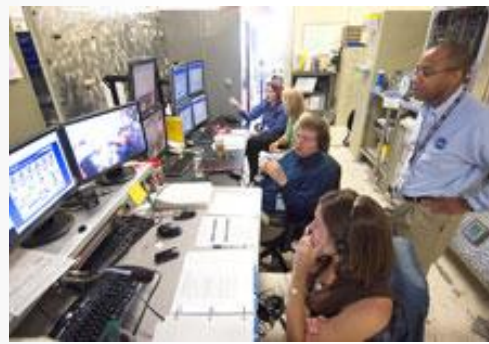
CO₂ Capture for Space Applications

Hamilton-Sundstrand is NASA's prime contractor for CO₂ capture in space

- CAMRAS: CO₂ And Moisture Removal Amine Swing bed
- Prototype delivered to NASA JSC (currently TRL6)
- Baselined for Orion; Lunar Lander; and new space suit
- Regeneration by space vacuum (heat for Mars environment)
- Heat exchange between adsorption/desorption maintains system isothermal



HS solid amine sorbent
in metal foam



Volunteers and NASA JSC scientists testing the CAMRAS system



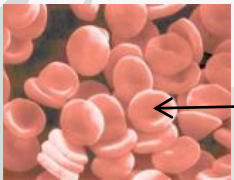
Prototype CAMRAS system

Carbonic Anhydrase: Nature's Solution

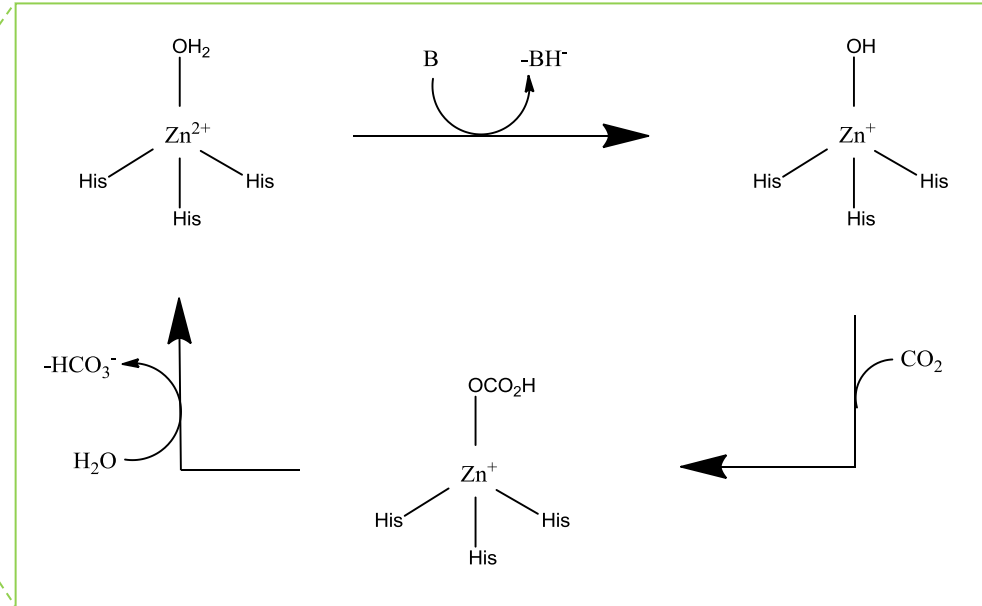
What we can learn from the enzyme: reactive, coordinated ZnOH site

Active site's fast, reversible interaction with CO₂

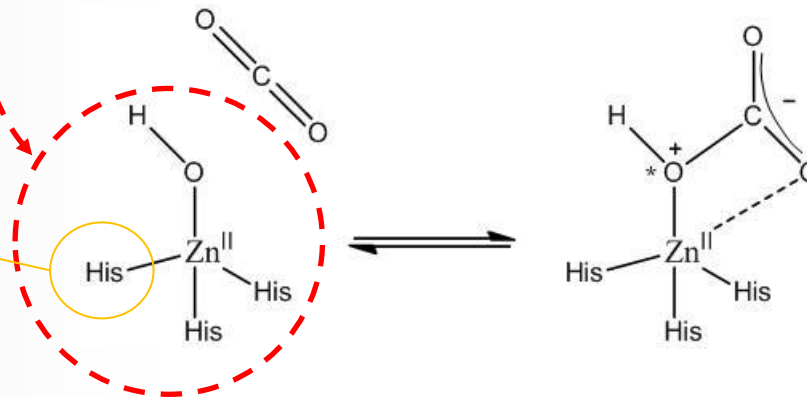
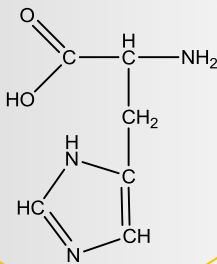
Red blood cells



Carbonic anhydrase

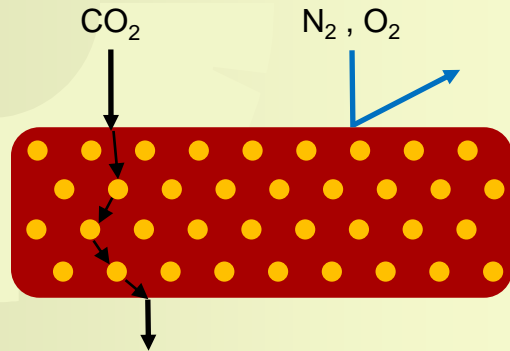


Histidine
(an amino acid)



Proposed Approach: Membrane-based Separation

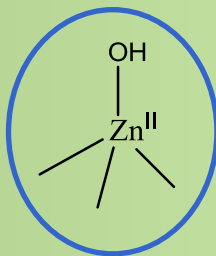
CO₂ transport facilitated by carriers mimicking enzyme active site



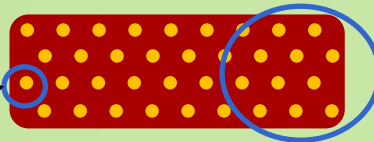
“Ideal” membrane:

- CO₂ transport is facilitated by specialized “carriers” within a barrier film
- Requires sites exhibiting fast and reversible interaction with CO₂

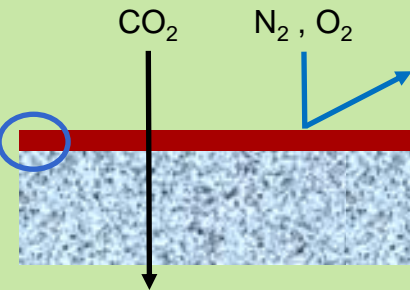
Proposed approach:



Thin polymer film containing CA-mimicking sites...



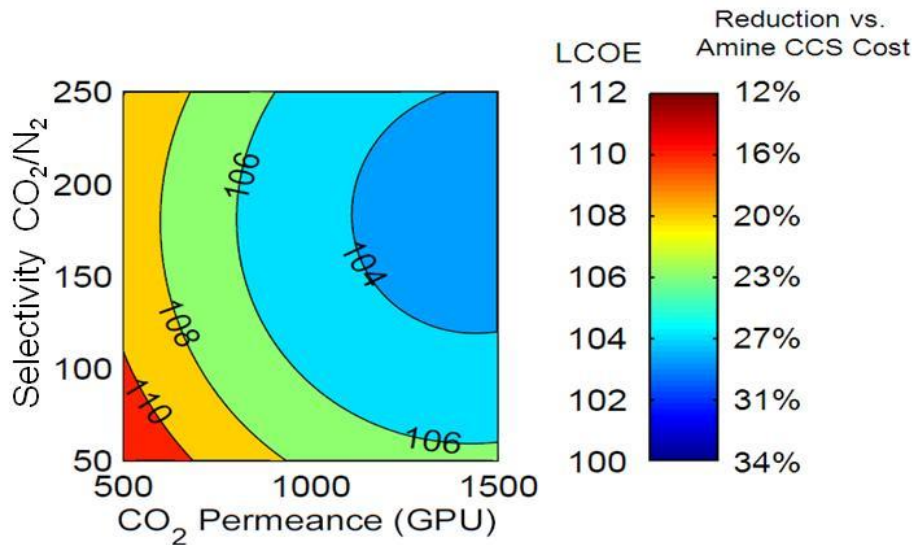
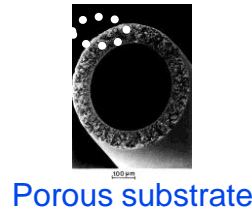
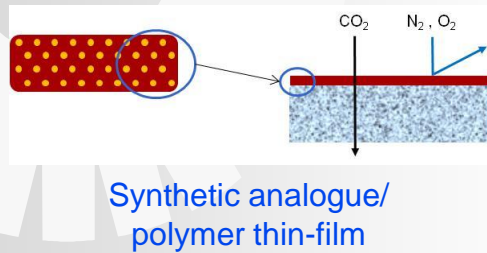
...supported on a microporous substrate



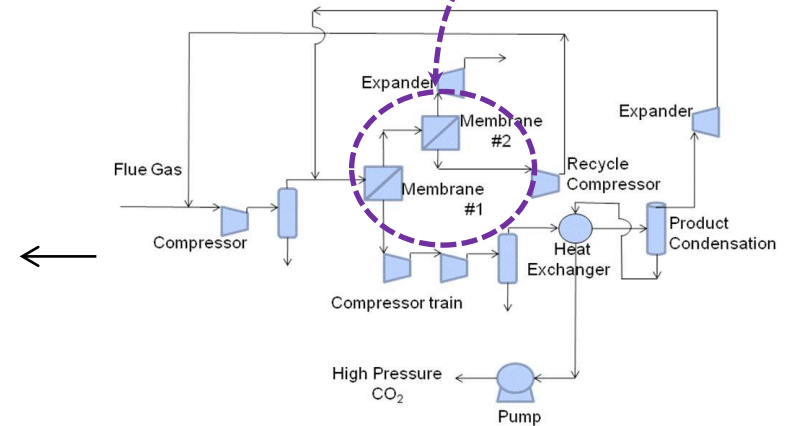
- ~30% lower CO₂ capture cost compared to liquid amines
- ~2 billion tons/yr CO₂ from existing coal-fired power plants
- Modular, skid-mounted configurations; no moving parts
- Flexibility to start with smaller system, gradually increase to 90% CO₂ capture

Separation System Feasibility Study

Simulation compares membrane vs. benchmark amine system



Membrane properties mapping



Simulated separation system (simplified)

Resistance to Flue Gas Contaminants: Experiments

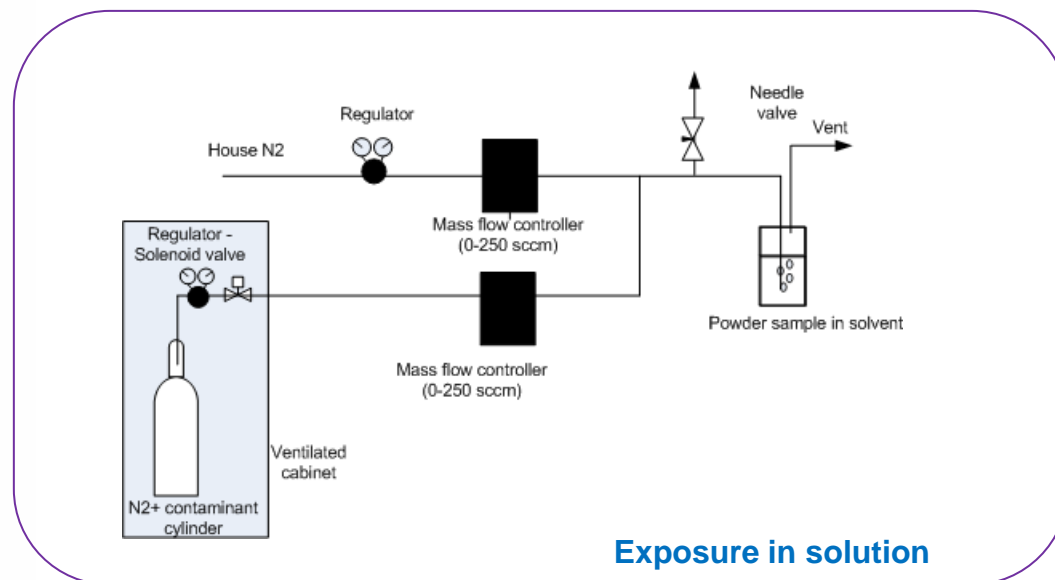
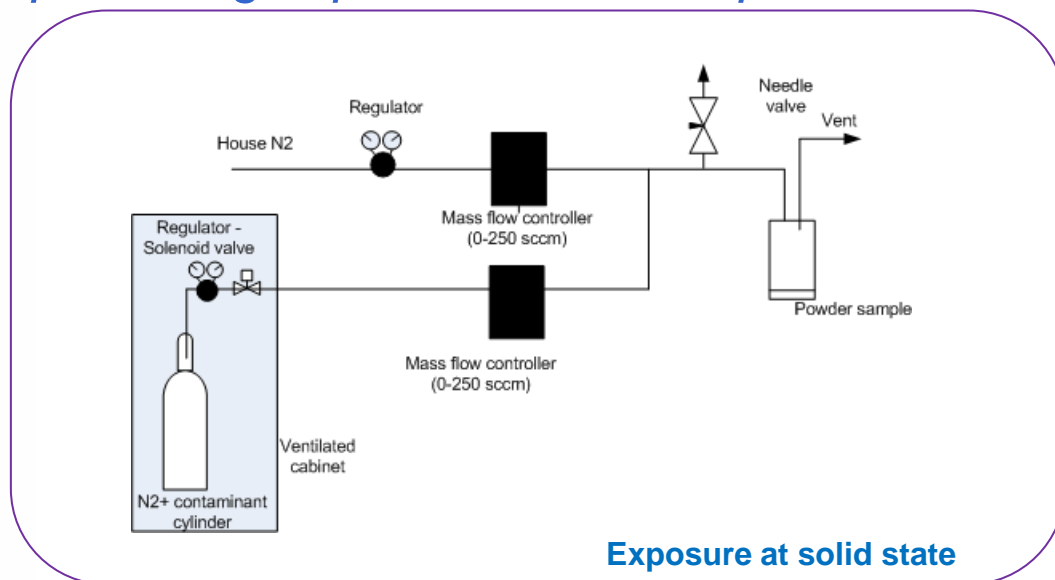
Analogue (powder) exposed in liquid and gas phase at max. expected levels

| Coal Type | SO ₂ | NO ₂ | NO | HCl |
|----------------|-----------------|-----------------|------|------|
| Sub-bituminous | 27.7 | 4.0 | 76.0 | 0.28 |
| Bituminous "A" | 78.5 | 4.3 | 81.7 | 3.44 |
| Bituminous "B" | 55.5 | 4.5 | 85.7 | 4.15 |
| Bituminous "C" | 38.2 | 3.3 | 61.8 | 9.9 |
| Lignite "A" | 68.2 | 3.5 | 67.3 | 0.34 |
| Lignite "B" | 123.8 | 4.5 | 84.6 | 0.03 |

(Highest concentration at each coal type noted in red)



SO₂: 125ppm & 12ppm
 NO₂: 35ppm (~10X)
 NO: 85ppm
 HCl: 10ppm, ~50% RH

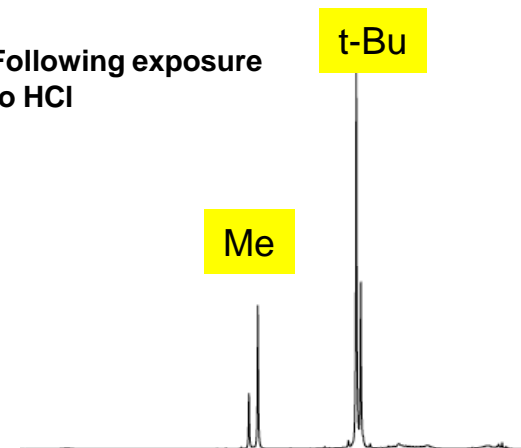


Exposure to Flue Gas Contaminants: Results

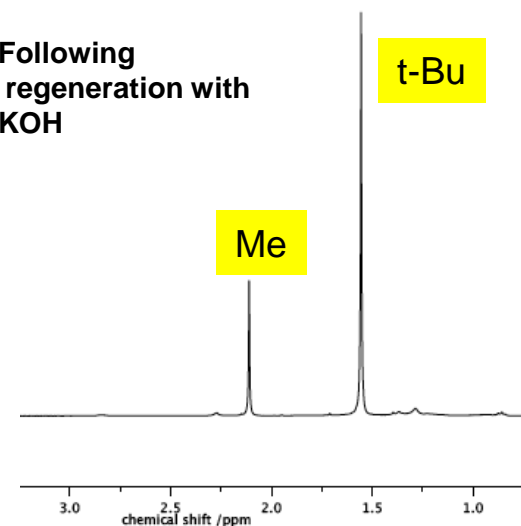
Interactions with NO_2 , SO_2 & HCl possible but reversible

- No evidence of structural or active site degradation
- Shifts in NMR & XPS (Zn) peaks observed with SO_2 , NO_2 & HCl but not with NO .
- Original NMR peaks restored following treatment in liquid phase (KOH) and gas phase.

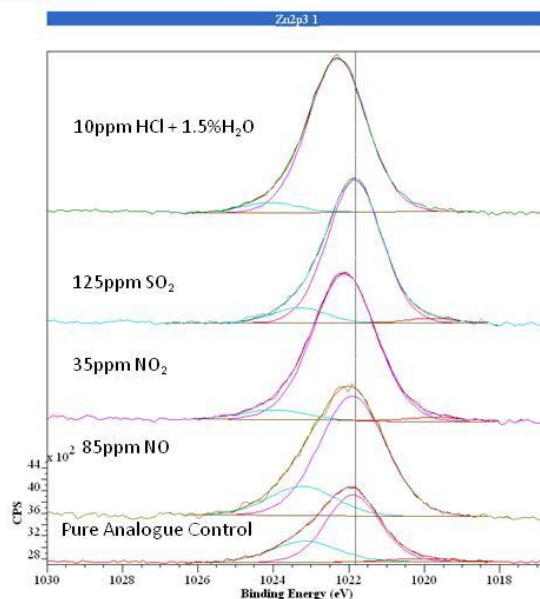
Following exposure to HCl



Following regeneration with KOH



**Zinc binding energy shifts
(indicating active site stability)**



**^1H NMR spectra of $[\text{Tp}^{\text{But,Me}}]\text{ZnOH}$
following exposure to HCl**

Key Findings to Date:

A separation system based on a membrane having both high selectivity and permeance can compare favorably to current benchmark (liquid amines)

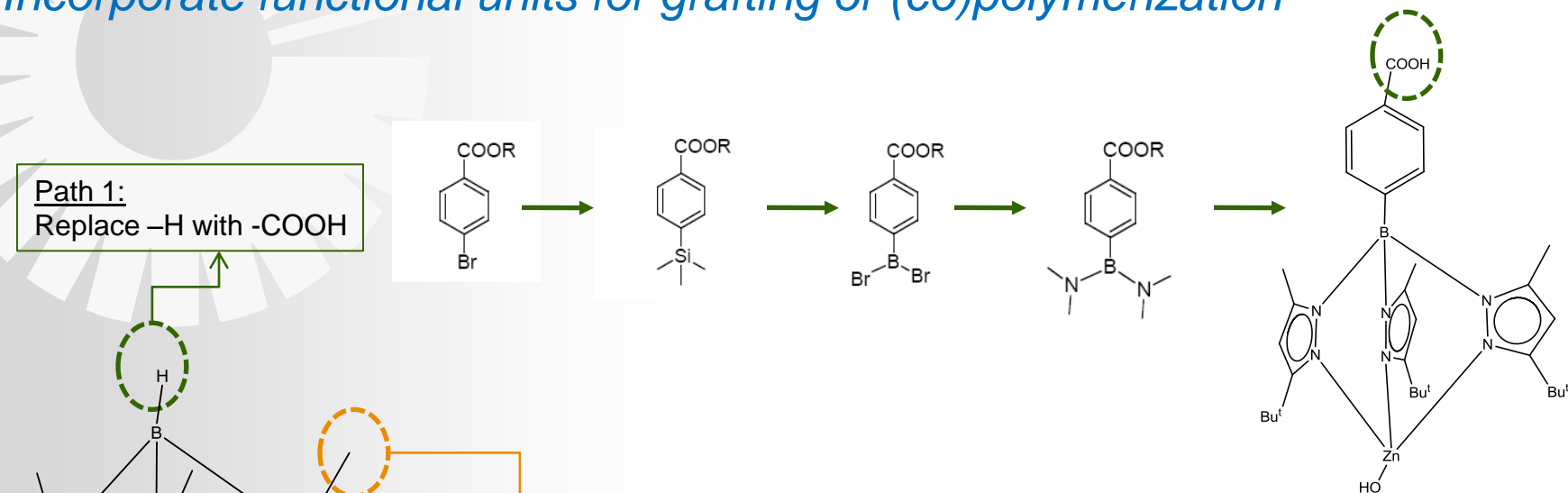
Three of the four main flue gas contaminants could form a reaction product with the synthetic analogue but the membrane can be regenerated

Incorporation of the ZnOH active site in the grafted synthetic analogue has proved more difficult than anticipated and has delayed progress.

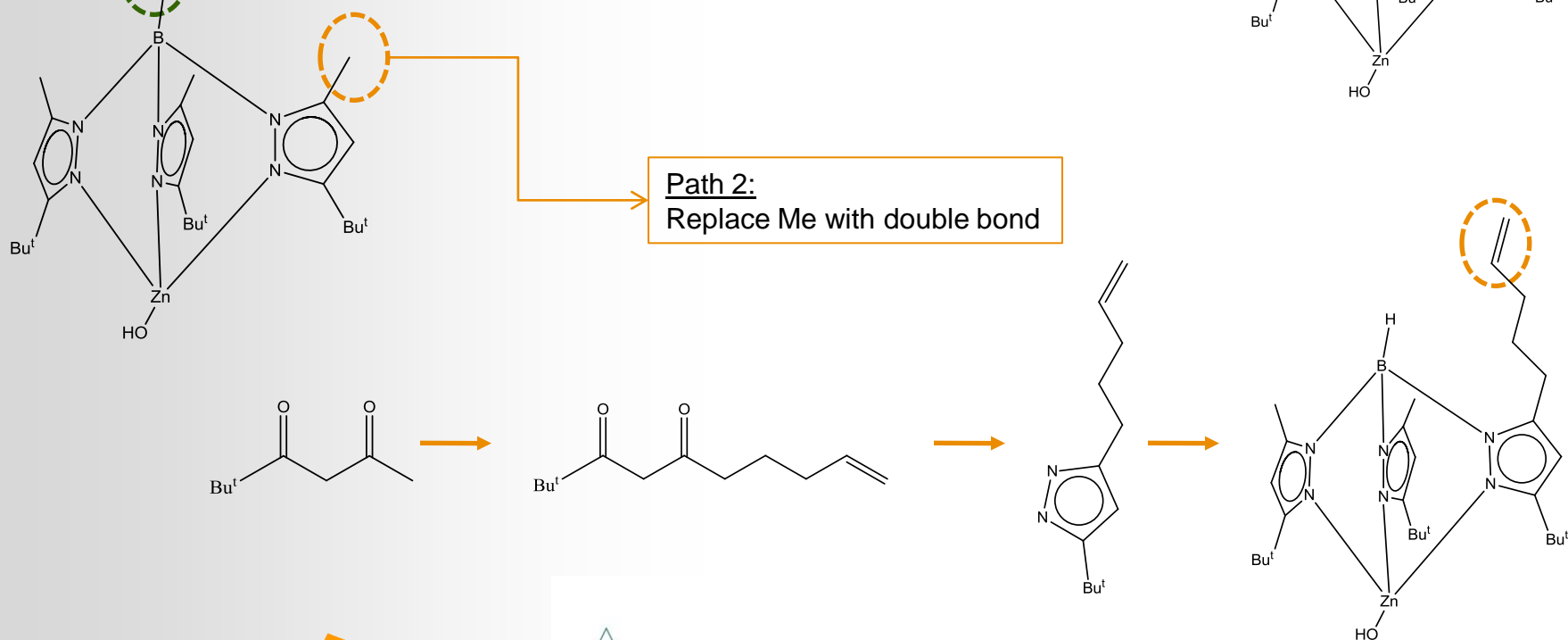
Synthetic Analogue Modification Examples

Incorporate functional units for grafting or (co)polymerization

Path 1:
Replace -H with -COOH



Path 2:
Replace Me with double bond



CO₂ Capture with Enzyme Synthetic Analogue

